Structure and Magnetism of Bis(propionato)-*p*-toluidinecopper(II), a Cupric Carboxylate Adduct with a One-Dimensional Polymeric Structure

D. B. W. Yawney, James A. Moreland, and Robert J. Doedens*

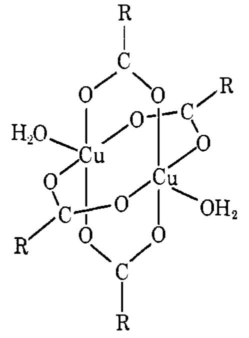
Contribution from the Department of Chemistry, University of California, Irvine, California 92664. *Received July 27, 1972*

Abstract: A novel polymeric structure has been established for the *p*-toluidine adduct of copper(II) propionate by a single-crystal X-ray structural analysis. Crystals of this compound are triclinic with a = 12.466 (7) Å, b = 12.183 (6) Å, c = 11.598 (6) Å, α = 116.03 (3)°, β = 91.73 (3)°, and γ = 73.82 (3)°. Observed and calculated densities are 1.36 (2) and 1.39 g/cm^3, respectively. The structure determination was based upon 1191 independent counter data; full-matrix least-squares refinement yielded a conventional R factor of 0.082. Evidence exists for some disorder of the ethyl carbon atoms. The crystal structure is composed of well-separated one-dimensional polymeric chains, extended along the a axis. Two crystallographically independent copper atoms are present, each of which is bound in a square-pyramidal configuration to four carboxylate oxygen atoms and to the nitrogen atom of a *p*-toluidine molecule. Two of the four independent carboxylate groups function as bidentate ligands and form triatomic bridges between the two independent copper atoms. The remaining two propionate groups form monatomic, centrosymmetric bridges between pairs of metal ions. Magnetic susceptibility data have been measured over the range 85–302°K; these data may be fit to the equation for an isolated pair of interacting ions of spin $^1/_2$. The magnetic results are interpreted in terms of a pairwise coupling model for the copper–copper interaction.

Copper(II) alkanoate monoadducts, $Cu(O_2CR)_2 \cdot L$, typically display room-temperature effective magnetic moments less than the spin-only value of 1.73 BM and an antiferromagnetic temperature dependence of their magnetic susceptibilities.[1] In general, the magnetic behavior of these adducts (and of the anhydrous copper(II) alkanoates) is well represented by eq 1, an expression for the magnetic susceptibility of an isolated pair of interacting ions of spin $^1/_2$.[3–6]

$$\chi_M'(\mathrm{Cu}) = \frac{g^2N\beta^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha \quad (1)$$

Cupric acetate monohydrate, for example, has a room temperature effective magnetic moment of 1.40 BM and the best fit of eq 1 to the observed χ_M' *vs.* T data is obtained for g = 2.13 and $2J$ = -284 cm^{-1}.[5] The negative value of $2J$ signifies an antiferromagnetic interaction, corresponding to a singlet ground state, separated by $2J$ from a triplet excited state. Thermal population of these two states leads to the observed magnetic susceptibility *vs.* temperature data.[7] The conformity of copper(II) acetate monohydrate to this magnetic model is readily understandable in view of its dimeric structure (I, R = CH_3).[12] This structure has also been found for adducts of copper(II) acetate with pyridine,[13,14] quinoline,[15] and thiocyanate,[16] as well as for adducts of other carboxylates.[17–21]



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[1] Magnetic properties of copper(II) carboxylates and related systems have been discussed in several recent reviews: M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964); C. Oldham, *Progr. Inorg. Chem.*, 10, 223 (1968); R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., University Press, Cambridge, England, 1968, pp 175–231; W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, **5**, 47 (1969); G. F. Kokoszka and G. Gordon, *ibid.*, **5**, 181 (1969). An extensive tabulation of magnetic data for copper(II) alkylcarboxylates has recently appeared.[2]

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(6) In this equation, $\chi_M'(\mathrm{Cu})$ is the molar paramagnetic susceptibility per Cu^{2+} ion and the parameters specific to a particular system are the g factor and $2J$, the energy level separation resulting from the spin–spin interaction.

(7) Jotham and Kettle[8] have proposed that an excited singlet state may be of importance in accounting for the magnetic properties of binuclear copper(II) alkanoate derivatives; others have suggested that existing magnetic data are insufficient to confirm the existence of such a state.[9–11]

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Many other copper(II) alkanoate monoadducts (and also most of the anhydrous alkanoates) exhibit magnetic properties similar to those of the monohydrate. The bulk of these adducts have μ_{eff} and $2J$ values close to those found for the monohydrate. Thus a recent tabulation[2] lists 20 cupric alkanoate monoadducts and six anhydrous alkanoates with best-fit $2J$ values (based upon eq 1) ranging from 278 to 358 cm^{-1}. An apparent exception to this rather small dependence of the degree of Cu–Cu interaction on the identity of L occurs for L = aniline or substituted aniline. These addends form complexes of the $Cu(O_2CR)_2 \cdot L$ stoichiometry which display magnetic susceptibility behavior in conformity with eq 1, but with Cu–Cu coupling of substantially smaller magnitude. Kokot and Martin, who carried out the initial magnetic investigations of adducts of aniline-type bases, reported typical g and $2J$ values of 2.18 and -101 cm^{-1}, respectively.[22] These parameters give rise to a room temperature μ_{eff} of $\sim$1.75 BM, slightly greater than the spin-only value but less than is usually observed for magnetically dilute Cu(II) complexes.

In order to determine whether any structural basis exists for this exceptional magnetic behavior, we decided to carry out an X-ray structural determination for a copper(II) alkanoate adduct of aniline or a related base. Many of these adducts are unstable or poorly crystalline; however we were able to obtain suitable crystals of the *p*-toluidine adduct of cupric propionate under anhydrous conditions. A preliminary report of the structural results has appeared;[23] we now report full details of the structural study together with the results of a magnetic investigation.

Experimental Section

Preparation of the Complex. Anhydrous cupric propionate (2.1 g, 0.005 mol) and *p*-toluidine (1.2 g, 0.011 mol) were suspended in 100 ml of toluene. The light green mixture was warmed gently with stirring and then filtered. The solution obtained was concentrated under a stream of N_2, stoppered, and cooled overnight at $-10°$. The green precipitate was filtered and dried over P_2O_5. Recrystallization at $-5°$ from acetone containing a slight excess of *p*-toluidine yielded long plate-like dark green crystals of $Cu(O_2CC_2H_5)_2 \cdot p\text{-}CH_3C_6H_4NH_2$. C, H, and N analyses were performed by Chemalytics, Inc., of Tucson, Ariz. Cu was determined locally by neutron activation analysis. *Anal.* Calcd for $CuC_{13}H_{19}NO_4$: Cu, 20.07; C, 49.33; H, 6.00; N, 4.42. Found: Cu, 19.77; C, 49.33; H, 6.14; N, 4.33. The visible spectrum was obtained on a Cary 14 spectrophotometer in C_6H_6 and shows: 0.005 *M*, 3850 Å, ϵ 289; 6900 Å, ϵ 136; 0.002 *M*, 3500–4300 Å (sh), $\epsilon \sim 120$; 6900 Å, ϵ 105.

Collection and Reduction of the X-Ray Data. Precession and Weissenberg photographs of several crystals of cupric propionate·*p*-toluidine showed no evidence of monoclinic or higher symmetry; a Delaunay reduction confirmed the assignment of this material to the triclinic crystal system. Lattice parameters (23°, λ (Cu $K\alpha_1$) 1.54051 Å) were obtained by least-squares refinement of the setting angles of 12 reflections which had been accurately centered on a Picker four-circle X-ray diffractometer. The three shortest noncoplanar lattice translations define a unit cell with a = 12.466 (7) Å, b = 12.183 (6) Å, c = 11.598 (6) Å, α = 116.03 (3)°, β = 91.73 (3)°, and γ = 73.82 (3)°. The numbers in parentheses are the least-squares standard deviations of the setting angles. The density of 1.36 (2) g/cm³ obtained by flotation in benzene–carbon tetrachloride solutions agrees satisfactorily with the calculated density of 1.39 g/cm³. Satisfactory solution and refinement of the structure was achieved in the centrosymmetric space group $P\bar{1}$.

An elongated plate-like crystal of dimensions 0.32 × 0.15 × 0.10 mm was employed for the collection of intensity data. The shortest dimension of the crystal was perpendicular to the well-developed $\{01\bar{2}\}$ faces; the long and short side faces were $\{010\}$ and $\{210\}$, respectively. Narrow-source, open-counter ω scans through several reflections displayed an average full width at half-maximum of 0.16°, indicative of suitably low mosaic spread.[24] Data were collected with Cu $K\alpha$ radiation by procedures similar to those previously described.[25] The diffracted beam was filtered through 0.0005-in. nickel foil; the takeoff angle was 2.5°. The counter aperture measured 5 × 5 mm and was positioned 24 cm from the crystal. The pulse-height analyzer was set to admit $\sim$90% of the Cu $K\alpha$ peak. Data were collected by the θ–2θ scan method with a symmetric scan range of $\pm 1.0°$ in 2θ from the calculated scattering angle. The scan rate was 1.0 deg/min, and stationary crystal–stationary counter background counts of 10 sec were taken at each end of the scan. Copper foil attenuators were inserted into the incident beam whenever the count rate exceeded $\sim 10^4$ counts/sec; a total of six reflections required attenuation. The intensities of all independent reflections with $2\theta \leq 85°$ were measured; beyond this 2θ value very few reflections had intensities significantly above background. For reflections with $2\theta \leq 50°$, the $\overline{hkl}$ form was also collected. Intensities of four standard reflections were measured periodically throughout data collection and showed no significant variations.

Processing of the intensity data was carried out by previously described methods.[25,26] The p factor in the expression for the standard deviations was assigned a value of 0.05. In averaging the two forms of reflections with $2\theta \leq 50°$, the standard deviation of the average intensity was taken as the larger of two estimates—one an average of the two individual σ's and the other an estimate based on the discrepancy between the two measured intensities. A total of 2650 data were collected; these consisted of 2031 independent data and 519 $\overline{hkl}$ reflections. A total of 1191 reflections had $F^2 > 3\sigma(F^2)$ and were employed in the final refinement. An absorption correction was applied to the observed intensities. Based upon a linear absorption coefficient of 21.2 cm^{-1}, the calculated transmission factors ranged from 0.74 to 0.87.

Solution and Refinement of the Crystal Structure. Initial values of the coordinates of the nonhydrogen atoms were obtained by conventional heavy-atom Patterson and difference Fourier techniques. Refinement was carried out by full-matrix least-squares methods, with the phenyl rings treated as rigid groups (C–C = 1.39 Å, $\angle$C–C–C = $\angle$H–C–C = 120°, C–H = 1.0 Å). Early in the course of the determination and refinement of the atomic coordinates, it became evident that several of the carbon atoms of the ethyl groups were subject to disorder. This problem was particularly acute for the ethyl group bound to C(4); its symptoms included the appearance on difference maps of chemically reasonable alternative atomic positions, high-thermal parameters, and bond distances which deviated somewhat from their expected values. Attempts to further define this problem were made by calculation of difference maps based upon F_c values which did not include the contributions of the suspect groups and by refinement of various fractional atom models for the disorder. Of several such models explored, only one yielded significant improvement over an ordered model in which the two largest chemically reasonably peaks in the vicinity of each ethyl group were taken as carbon atoms. The disordered model included two alternatives for C(6), each weighted as 50% of a full carbon atom. This equal weighting was based on the nearly equal peak heights observed on difference maps. Discrepancy factors at convergence for the three fully refined models were the following: ordered model, isotropic thermal parameters for all atoms, R_1 = 0.116, R_2 = 0.136; ordered model, copper atoms

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(26) Programs employed in this structural analysis included local versions of PICK (J. A. Ibers), for cell refinement and generation of diffractometer settings; PICKOUT (R. J. Doedens, J. A, Ibers), for data processing; GONO (W. C. Hamilton), for absorption correction; FORDAP (A. Zalkin), for Fourier summation; UCIGLS (derived from Busing, Martin, and Levy's ORFLS), for structure factor calculations and least-squares refinement; ORFFE (Busing, Martin, and Levy), for function and error calculations; PLANET (D. L. Smith), for least-squares plane calculations; DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson), for preparation of figures; and RSCAN (R. J. Doedens), for evaluation of the weighting scheme. All computations were carried out on the local PDP-10 computer.

Table I. Atomic Positional and Thermal Parameters for $Cu(O_2CC_2H_5)_2 \cdot p\text{-}CH_3C_6H_4NH_2$

Atom	x	y	z	B, Å^2
Cu(1)	0.1343 (2)[a]	−0.0387 (3)	0.0159 (3)	
Cu(2)	0.3630 (2)	0.0365 (3)	0.0426 (3)	
O(1)	0.2291 (12)	−0.1436 (12)	0.0850 (12)	5.6 (3)
O(2)	0.3938 (11)	−0.1321 (13)	0.0377 (13)	6.0 (4)
O(3)	0.1068 (12)	0.1113 (13)	0.1800 (14)	6.1 (4)
O(4)	0.2828 (11)	0.1223 (12)	0.2122 (12)	5.3 (3)
O(5)	0.0365 (11)	0.0596 (12)	−0.0617 (12)	5.5 (4)
O(6)	0.1714 (14)	0.1355 (14)	−0.0771 (14)	7.8 (4)
O(7)	0.4498 (11)	−0.0346 (12)	−0.1183 (13)	5.0 (3)
O(8)	0.3398 (14)	−0.1368 (14)	−0.2462 (15)	8.2 (4)
N(1)	0.1568 (12)	−0.1863 (14)	−0.1652 (14)	4.6 (4)
N(2)	0.3551 (12)	0.2052 (14)	0.0359 (15)	4.9 (4)
C(1)	0.3349 (20)	−0.1800 (21)	0.0752 (21)	6.1 (6)
C(2)	0.3988 (23)	−0.2861 (26)	0.1135 (26)	9.9 (8)
C(3)	0.3309 (26)	−0.3544 (28)	0.1378 (28)	11.8 (9)
C(4)	0.1767 (21)	0.1585 (23)	0.2492 (24)	6.7 (6)
C(5)	0.1269 (30)	0.2719 (36)	0.3922 (38)	12.1 (11)
C(6a)	0.1977 (60)	0.3054 (67)	0.4657 (70)	16.1 (23)
C(6b)	0.1458 (64)	0.2154 (71)	0.4537 (75)	16.1 (24)
C(7)	0.0752 (22)	0.1258 (23)	−0.1080 (23)	7.1 (6)
C(8)	0.0068 (22)	0.1839 (26)	−0.1813 (28)	9.0 (7)
C(9)	0.0216 (27)	0.0881 (31)	−0.3095 (33)	13.0 (10)
C(10)	0.4167 (20)	−0.0899 (22)	−0.2255 (24)	6.7 (6)
C(11)	0.4797 (21)	−0.0916 (23)	−0.3436 (27)	8.7 (7)
C(12)	0.4372 (32)	−0.1385 (35)	−0.4686 (38)	16.0 (12)
C(19)	0.2976 (21)	−0.7055 (24)	−0.2280 (24)	8.7 (7)
C(26)	0.1949 (21)	0.6940 (23)	0.4914 (23)	8.5 (7)

Anisotropic Thermal Parameters × 10^5 [b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	782 (31)	1842 (53)	2328 (59)	−430 (30)	−217 (30)	1133 (45)
Cu(2)	972 (33)	1765 (51)	1855 (51)	−550 (31)	75 (30)	706 (38)

Group Parameters[c]

	x	y	z	ϕ	θ	ρ
Ring 1	0.2215 (8)	−0.4393 (10)	−0.1994 (8)	106.95 (54)	−171.95 (46)	5.14 (45)
Ring 2	0.2789 (9)	0.4418 (9)	0.2594 (9)	88.08 (53)	156.79 (54)	−120.66 (51)

[a] Numbers in parentheses in tables and in the text are estimated standard deviations in the least significant figure. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] The coordinates x, y, and z are the fractional coordinates of the center of gravity of the group; the angles ϕ, θ, and ρ are the three rotation angles defined in: R. J. Doedens in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 198–200.

anisotropic, R_1 = 0.083, R_2 = 0.103; disordered model, copper atoms anisotropic, R_1 = 0.082, R_2 = 0.101. Further refinement following correction of a minor error in the data yielded the final discrepancy factors of 0.081 and 0.100. In the final cycle of refinement no parameter shift was greater than 0.5σ, with the exception of several parameters of the disordered ethyl group which were undergoing poorly damped oscillations of 0.6–2.0σ. Since the parameters of this ethyl group are not well-known in any event and are not strongly correlated with any parameters of interest, refinement was terminated at this point. An R-factor ratio test[27] indicated that the disordered model for C(6) was a significant improvement over the ordered model at a confidence level greater than 99%.

In the least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. The final standard deviation of an observation of unit weight was 2.5. Calculation of mean $w(\Delta F)^2$ values for subsets of the data as a function of uncorrected intensity, observed F, and Bragg angle showed no significant trends. Calculation of structure factors for data with $F_o < 3\sigma(F_o)$ showed only seven reflections with $|\Delta F|/\sigma(F_o) \geq 3$. Scattering factors for Cu, O, N, and C were taken from ref 28 and those of Stewart, *et al.*,[29] were employed for H. Structure factor calculations included provisions for the real and imaginary parts of anomalous scattering by the copper atom.[30]

Final atomic positional and thermal parameters are tabulated in Table I; derived parameters of the group atoms are given in Table II. Intramolecular distances and angles are summarized in Tables III and IV, respectively. A table of observed and calculated structure factors is available.[31]

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured by the Faraday method by use of an Alpha Model 1402 magnetic susceptibility system equipped with an Alpha/Ainsworth Model 1071 electronic balance and an Alpha Model 1424 variable-temperature accessory system. Measurements were made at a field strength of *ca.* 8000 G on a powdered sample under nitrogen. The calibrant employed was $HgCo(NCS)_4$, the magnetic susceptibility of which was taken as 16.44 × 10^{-6} cgs units at 20°. A diamagnetic correction of −169.38 × 10^{-6} cgs units was calculated from Pascal's constants. The effective magnetic moment was calculated from the equation $\mu_{\text{eff}} = 2.83[(\chi_M' - N\alpha)T]^{1/2}$, where $N\alpha$ was given the value of 60 × 10^{-6} cgs units. The observed magnetic susceptibility data were fitted to eq 1. In the fitting procedure, all experimentally observed susceptibilities were equally weighted and the "best" values of g and $2J$ were taken to be those which minimized $\Sigma(\chi_M'(\text{obsd}) - \chi_M'(\text{calcd}))^2$. The magnetic data are given in Table V.

Results

Description of the Structure. The crystal structure of

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(31) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1164. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table II. Coordinates and Thermal Parameters of Group Atoms[a]

	x	y	z	B, Å^2
		Group 1		
C(13)	0.1889 (14)	−0.3142 (11)	−0.1835 (12)	5.5 (5)
C(14)	0.3012 (12)	−0.3872 (15)	−0.2194 (13)	6.4 (6)
C(15)	0.1092 (9)	−0.3663 (14)	−0.1635 (13)	6.0 (6)
C(16)	0.3337 (10)	−0.5124 (15)	−0.2353 (14)	7.6 (7)
C(17)	0.1418 (13)	−0.4914 (15)	−0.1793 (14)	7.2 (6)
C(18)	0.2540 (15)	−0.5645 (11)	−0.2152 (14)	8.4 (7)
H(1)	0.3584 (16)	−0.3498 (22)	−0.2338 (20)	b
H(2)	0.0286 (10)	−0.3138 (20)	−0.1377 (19)	
H(3)	0.4143 (11)	−0.5649 (21)	−0.2611 (20)	
H(4)	0.0846 (17)	−0.5289 (21)	−0.1649 (21)	
		Group 2		
C(20)	0.3165 (13)	0.3255 (11)	0.1492 (11)	5.3 (5)
C(21)	0.3908 (9)	0.3684 (14)	0.2385 (15)	6.3 (6)
C(22)	0.2047 (12)	0.3990 (12)	0.1701 (14)	6.4 (6)
C(23)	0.3532 (13)	0.4847 (14)	0.3487 (13)	7.3 (6)
C(24)	0.1670 (9)	0.5153 (14)	0.2804 (16)	7.5 (6)
C(25)	0.2413 (14)	0.5582 (11)	0.3696 (12)	8.1 (7)
H(5)	0.4711 (10)	0.3156 (20)	0.2235 (23)	
H(6)	0.1514 (16)	0.3682 (20)	0.1060 (19)	
H(7)	0.4065 (18)	0.5155 (20)	0.4129 (18)	
H(8)	0.0867 (11)	0.5681 (21)	0.2954 (24)	

[a] The positional parameters and their estimated standard deviations were derived from the group parameters given in Table I. Since the group geometry was fixed, the tabulated standard deviations may not be used to estimate errors in distances or angles within a group. [b] Group hydrogen atoms were assigned temperature factors of 8.5.

Table III. Bond Distances and Selected Intrachain Nonbonded Contacts (Å)[a]

	(a) Copper Coordination Spheres		
Cu(1)–O(1)	1.917 (14)	Cu(2)–O(2)	1.957 (14)
Cu(1)–O(3)	1.928 (15)	Cu(2)–O(4)	1.921 (14)
Cu(1)–O(5)	1.948 (14)	Cu(2)–O(7)	1.893 (13)
Cu(1)–N(1)	2.040 (15)	Cu(2)–N(2)	2.065 (15)
Cu(1)–O(5)′	2.318 (13)	Cu(2)–O(7)′	2.465 (14)
	(b) Carboxylate Groups		
O(1)–C(1)	1.26 (2)	O(2)–C(1)	1.24 (2)
O(3)–C(4)	1.25 (2)	O(4)–C(4)	1.29 (2)
O(5)–C(7)	1.34 (2)	O(7)–C(10)	1.25 (2)
O(6)–C(7)	1.26 (2)	O(8)–C(10)	1.21 (2)
C(1)–C(2)	1.55 (3)	C(7)–C(8)	1.45 (3)
C(2)–C(3)	1.45 (3)	C(8)–C(9)	1.41 (3)
C(4)–C(5)	1.62 (4)	C(10)–C(11)	1.59 (3)
C(5)–C(6a)	1.24 (9)	C(11)–C(12)	1.45 (4)
C(5)–C(6b)	1.17 (8)		
	(c) *p*-Toluidine Molecules		
N(1)–C(13)	1.41 (2)	N(2)–C(20)	1.44 (2)
C(18)–C(19)	1.59 (3)	C(25)–C(26)	1.59 (2)
	(d) Nonbonded Contacts		
Cu(1)···Cu(2)	3.197 (4)	O(6)···N(2)	2.76 (2)
Cu(1)···Cu(1)′	3.272 (6)	O(8)···N(1)	2.80 (2)
Cu(2)···Cu(2)′	3.341 (6)	O(2)···N(2)′	3.04 (2)
Cu(1)···O(6)	2.91 (2)	O(6)···O(8)	3.15 (2)
Cu(2)···O(6)	2.96 (2)		
Cu(2)···O(8)	3.14 (2)		

[a] In all tables and in the text, primes denote atoms related to those in the asymmetric unit by a crystallographic center of symmetry.

Table IV. Bond Angles (deg)

O(1)–Cu(1)–O(3)	91.6 (6)	O(2)–Cu(2)–O(4)	92.8 (6)
O(1)–Cu(1)–O(5)	176.9 (6)	O(2)–Cu(2)–O(7)	91.4 (6)
O(1)–Cu(1)–N(1)	93.3 (6)	O(2)–Cu(2)–N(2)	171.5 (6)
O(1)–Cu(1)–O(5)′	98.7 (5)	O(2)–Cu(2)–O(7)′	86.0 (5)
O(3)–Cu(1)–O(5)	90.9 (5)	O(4)–Cu(2)–O(7)	174.0 (6)
O(3)–Cu(1)–N(1)	174.7 (6)	O(4)–Cu(2)–N(2)	93.5 (6)
O(3)–Cu(1)–O(5)′	88.3 (5)	O(4)–Cu(2)–O(7)′	95.3 (5)
O(5)–Cu(1)–N(1)	83.9 (6)	O(7)–Cu(2)–N(2)	81.9 (6)
O(5)–Cu(1)–O(5)′	80.2 (6)	O(7)–Cu(2)–O(7)′	80.7 (6)
N(1)–Cu(1)–O(5)′	92.0 (5)	N(2)–Cu(2)–O(7)′	87.7 (5)
Cu(1)–O(1)–C(1)	127.9 (15)	Cu(2)–O(2)–C(1)	131.8 (15)
Cu(1)–O(3)–C(4)	128.6 (16)	Cu(2)–O(4)–C(4)	131.2 (16)
Cu(1)–O(5)–C(7)	121.1 (15)	Cu(2)–O(7)–C(10)	124.7 (15)
Cu(1)–O(5)–Cu(1)′	99.8 (6)	Cu(2)–O(7)–Cu(2)′	99.3 (6)
Cu(1)–O(5)′–C(7)′	138.6 (15)	Cu(2)–O(7)′–C(10)′	133.8 (15)
Cu(1)–N(1)–C(13)	120.5 (12)	Cu(2)–N(2)–C(20)	120.6 (13)
O(1)–C(1)–O(2)	122.6 (23)	O(3)–C(4)–O(4)	123.9 (24)
O(1)–C(1)–C(2)	121.0 (22)	O(3)–C(4)–C(5)	116.0 (24)
O(2)–C(1)–C(2)	116.4 (23)	O(4)–C(4)–C(5)	120.2 (24)
O(5)–C(7)–O(6)	113.8 (23)	O(7)–C(10)–O(8)	126.5 (24)
O(5)–C(7)–C(8)	120.6 (24)	O(7)–C(10)–C(11)	115.2 (23)
O(6)–C(7)–C(8)	125.5 (25)	O(8)–C(10)–C(11)	118.2 (24)
C(1)–C(2)–C(3)	115.7 (25)	C(4)–C(5)–C(6a)	115.4 (48)
C(7)–C(8)–C(9)	106.8 (27)	C(4)–C(5)–C(6b)	101.1 (59)
		C(10)–C(11)–C(12)	118.9 (27)
N(1)–C(13)–C(14)	119.7 (17)	N(2)–C(20)–C(21)	120.0 (13)
N(1)–C(13)–C(15)	120.3 (13)	N(2)–C(20)–C(22)	119.9 (13)
C(16)–C(18)–C(19)	117.5 (16)	C(23)–C(25)–C(26)	122.0 (15)
C(17)–C(18)–C(19)	122.4 (19)	C(24)–C(25)–C(26)	117.9 (14)

Table V. Magnetic Susceptibility Data[a]

T, °K	χ_M'(obsd)	μ_{eff}	χ_M'(calcd)
85	2353	1.24	2451
92.5	2453	1.33	2472
102.5	2453	1.40	2461
115	2423	1.47	2406
125	2333	1.51	2345
135	2303	1.56	2276
154	2152	1.61	2139
174	2033	1.66	1997
194	1882	1.68	1866
214	1792	1.72	1747
234	1642	1.72	1641
253	1552	1.74	1549
278	1432	1.75	1443
302.5	1342	1.76[b]	1351

[a] Observed susceptibility values listed are molar paramagnetic susceptibilities per Cu^{2+} ion in cgs units × 10^6; these values are subject to an estimated standard deviation of 15–20 units on the scale tabulated. Calculated susceptibilities are obtained from eq 1 with $g = 2.20$ and $2J = -105$ cm^{-1}. [b] The previously reported room temperature μ_{eff} value for this complex was in error.[23]

bis(propionato)-*p*-toluidinecopper(II) is composed of one-dimensional polymeric chains extended along the *a* axis. The chains are well separated, with a shortest interchain contact (excluding hydrogen atoms) of 3.47 Å. A portion of the structure of one chain, with ethyl and *p*-tolyl groups omitted for clarity, is shown in Figure 1. Two crystallographically independent copper atoms (labeled Cu(1) and Cu(2)) are present, each of which is bound in a square-pyramidal configuration to four carboxylate oxygen atoms and to the nitrogen atom of a *p*-toluidine molecule. Two of the four independent carboxylate groups function as bidentate ligands, bridging Cu(1) and Cu(2) in a syn,syn configuration. The remaining two propionate groups are monodentate and form monatomic oxygen bridges from a basal site of one copper atom to the apical site of its centrosymmetric equivalent. In the resulting chain structure the copper–copper vectors form a zig-zag line, with Cu(2)–Cu(1)–Cu(1)′ and Cu(1)–Cu(2)–Cu(2)′ angles of 147.5 (2) and 151.1 (2)°, respectively.

The two independent copper atoms Cu(1) and Cu(2) are linked in a manner reminiscent of the dimeric cupric acetate structure, but with two rather than four triatomic carboxylate bridges. One basal coordination

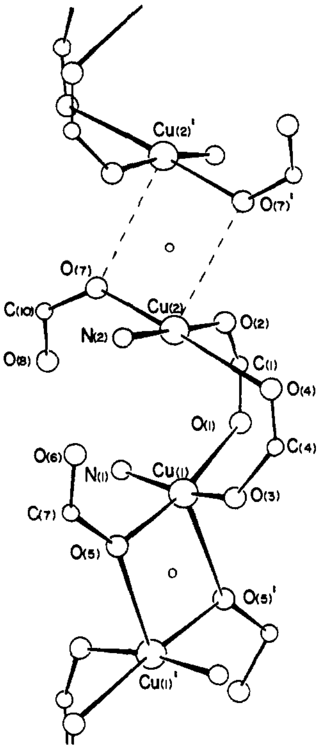

Figure 1. A portion of the linear chain structure of bis(propionato)-*p*-toluidinecopper(II). Ethyl and *p*-tolyl groups have been omitted for clarity. Atom labels not shown in the figure are defined as follows: ethyl carbon atoms are given numbers (1) (α-carbon) and (2) (β-carbon) units greater than the number of the corresponding carboxylate carbon atom; phenyl carbon atoms are numbered C(13)–C(18) and C(20)–C(25) with the lowest numbered carbon atom bound to the NH_2 group; hydrogen atoms (1)–(4) are bound to carbon atoms (14)–(17) and hydrogens (5)–(8) to carbons (21)–(24); the methyl carbon atoms are numbered 19 and 26.

site of each metal atom is occupied by the nitrogen atom of a *p*-toluidine molecule; a probable N–H···O hydrogen bond links this atom to the free oxygen atom of one monodentate propionate group. The two square-pyramidal copper coordination polyhedra are tilted so that their basal planes make a dihedral angle of 50.0° and the Cu(1)···Cu(2) distance is 3.197 (4) Å; these parameters may be compared with the parallel basal planes and Cu···Cu separation of *ca.* 2.6 Å found in the cupric acetate structure. The tilting of the copper coordination polyhedra is reflected in the Cu–O–C angles of the bidentate carboxylate groups; these angles have an average value of 130.0 (15)°, about 5° greater than is typically observed in complexes with the copper(II) acetate structure.

The linkages of Cu(1) and Cu(2) with their centrosymmetric equivalents are qualitatively similar, both consisting of a pair of monatomic oxygen bridges from a basal coordination site of one copper atom to the apical site of an adjacent metal atom and resulting in the sharing of an apical edge by the two square-pyramidal coordination polyhedra. We are aware of only one other instance in which a monodentate carboxylate group bridges two metal atoms in this fashion.[32] The Cu(2)–Cu(2)′ bridge is less symmetric than that between Cu(1) and Cu(1)′ as a consequence of a longer Cu–apical O bond (Cu(1)–O(5)′ = 2.318 (13) Å, Cu(2)–O(7)′ = 2.465 (14) Å). The Cu(1)–Cu(1)′ and Cu(2)–Cu(2)′ distances are 3.272 (6) and 3.341 (6) Å, respectively.

The coordination geometry about each copper atom is distorted square pyramidal. As can be seen from the results of least-squares plane calculations summarized in Table VI, Cu(1) lies in the plane defined by the atoms occupying its basal coordination sites, while Cu(2) is *below* (*i.e.*, on the opposite side to O(7)′) its basal plane by 0.08 Å. The apical O–Cu–basal atom angles about both copper atoms vary considerably—from 80.2 (6) to 98.7° for Cu(1) and from 80.7 (6) to 95.3 (5)° for Cu(2). In both cases the smallest such angle involves the centrosymmetric equivalent of the apical oxygen atom and the largest angle is associated with an oxygen atom of a triatomic bridging carboxylate group. Basal Cu–O distances vary over a normal range of 1.893 (13)–1.957 (14) Å and Cu–N distances are 2.040 (15) and 2.065 (15) Å.

Table VI. Least-Squares Planes[a]

(1) Plane Containing O(1), O(3), O(5), and N(1)
Equation of Plane: $0.9017X + 0.3611Y - 0.2377Z = 1.1531$
Distances to plane (Å)

O(1)	−0.019	N(1)	0.020
O(3)	0.020	Cu(1)	0.0005
O(5)	−0.021		

(2) Plane Containing O(2), O(4), O(7), and N(2)
Equation of Plane: $-0.8874X + 0.1468Y - 0.4370Z = -4.3578$
Distances to plane (Å)

O(2)	−0.015	N(2)	−0.015
O(4)	0.014	Cu(2)	0.082
O(7)	0.016		

[a] Unit weights were employed in the calculation of all planes. The equations of the planes are expressed with respect to coordinates (X, Y, Z) referred to an orthogonal system (A, B, C) oriented with respect to the crystallographic axes such that A is parallel to a, B is parallel to $c^* \times a$, and C is parallel to $A \times B$.

The C–O distances and O–C–O angles of the triatomic bridging carboxylate groups are normal, with average values of 1.26 (2) Å and 123.2 (24)°, respectively. In the monatomically bridging carboxylate groups the C–O distances range from 1.21 (2) to 1.34 (2) Å and the O–C–O angles are 113.8 (23) and 126.5 (24)°. The C–C distances of the ethyl groups (not including the C(5)–C(6) distances) average to 1.50 (3) Å; the variation of these distances is greater than usual, owing presumably to the high thermal motion and/or partial disorder of the ethyl carbon atoms.

Magnetic Results. In Figure 2, the magnetic data given in Table V are represented graphically. Included in this figure are the susceptibility data reported by Kokot and Martin for copper(II) butyrate·*p*-toluidine.[22] We regard their data as identical with ours within experimental error. Mabbs, *et al.*, have also reported magnetic susceptibility *vs.* temperature data for copper(II) propionate·*p*-toluidine;[33] their data show appreciable deviations from ours, particularly at low temperatures. The best fit of our magnetic data to the dimer equation occurs for $g = 2.20$ and $2J = -105$ cm^{-1}. These parameters are in very good agreement with Kokot and Martin's values ($g = 2.18$ and $2J =$

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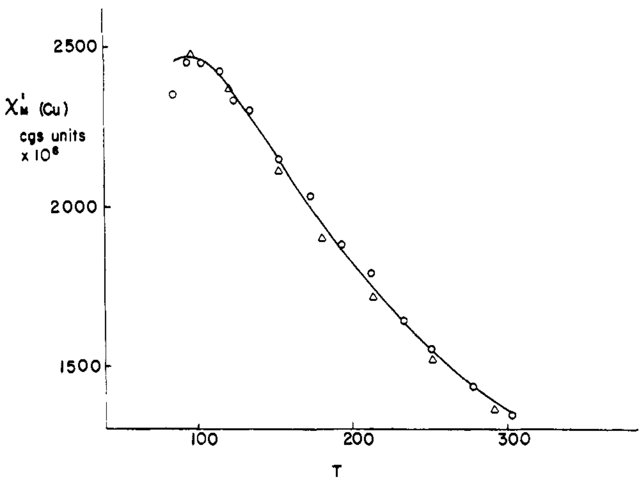

Figure 2. Magnetic susceptibility *vs.* T(°K) data. Open circles are experimental data points; triangles are data for cupric butyrate-*p*-toluidine from ref 22. The solid line represents the susceptibilities calculated from eq 1 with $g = 2.20$ and $2J = -105\ \text{cm}^{-1}$.

$-101\ \text{cm}^{-1}$) for the butyrate adduct. The g value for the propionate adduct has also been estimated by Ablov, *et al.*, on the basis of solid-state epr measurements.[34] These workers obtained the values $g_\perp = 2.045 \pm 0.01$ and $g_\parallel = 2.37 \pm 0.03$; corresponding to an average g of 2.15.

Discussion

Although the structure found for copper(II) propionate·*p*-toluidine was unexpected and unprecedented, it is in fact closely related to the crystal structure of anhydrous cupric propionate.[35] In the anhydrous salt, carboxylate-bridged dimers are linked into a chain structure by apical Cu–O interactions of length ~2.35 Å. The resulting structure, shown schematically in Figure 3, has a zig-zag chain of copper atoms much like that found in the present case. In the *p*-toluidine adduct, however, two of the four carboxylate bridges are broken and a *p*-toluidine molecule occupies a basal coordination site of each cupric ion. Freed of the constraints provided by the two broken carboxylate bridges, the two independent copper atoms spread apart in order to accommodate the addend molecule while retaining the other two triatomic bridges.

The reasons for the adoption of this structure in preference to the more common dimeric copper(II) acetate hydrate structure of identical stoichiometry are by no means clear and further experimental data will be required before resolution of this point is possible. Factors worthy of consideration include the presumed N–H···O hydrogen bonds, the steric requirements of the *p*-toluidine molecule, and possible preference of aniline-type bases for binding in basal rather than apical coordination sites.[36] On the basis of published magnetic susceptibility and epr studies,[22,34] it seems to us likely that many other copper(II) carboxylate adducts of substituted anilines adopt structures similar to that of copper(II) propionate·*p*-toluidine. It will be of interest to determine whether adducts of aliphatic amines also have this structure. Also of interest will be studies of the adduct in solution in an effort to determine the principal species present under various conditions and to correlate spectral and magnetic properties of the solutions. Such studies are now in progress in our laboratory.

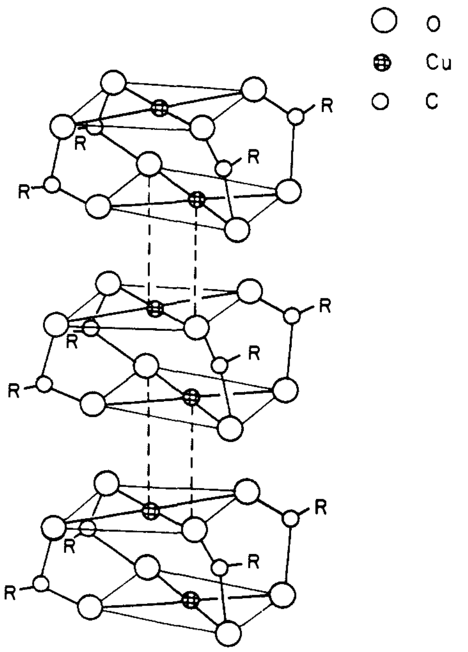

Figure 3. The structure of anhydrous copper(II) propionate, as reported in ref 35.

As is evident from Table V and Figure 2, the observed magnetic susceptibility data over the temperature range 85–302°K may be represented by the usual equation for an isolated pair of interacting ions of spin $^1/_2$. This behavior can most simply be accounted for by presuming the predominant interaction within the one-dimensional chain to be a pairwise one. This would not imply that additional magnetic interactions are absent, but only that such interactions, if present, are not large enough to significantly alter the magnetic susceptibility over the temperature range studied.

As usual, no direct experimental evidence exists which permits a definitive choice to be made from among the various modes of Cu–Cu interaction which could, in principle, exist in this complex. However, indirect evidence leads, in our view, to a persuasive interpretation of the observed magnetic properties. First, the long Cu–Cu distances (ranging from 3.197 (4) to 3.341 (6) Å) and the low symmetry of the individual ion pairs render a predominantly "direct" (*i.e.*, associated with overlap of orbitals on adjacent Cu^{2+} ions) metal–metal interaction unlikely. The shortest Cu···Cu contact is more than 0.5 Å longer than the Cu···Cu separation in cupric acetate hydrate, for which the mechanism of Cu–Cu interaction has been the subject of much debate. It seems highly improbable that a significant direct interaction could be maintained at a Cu–Cu separation as great as 3.2 Å. Granting this, one is left with the possibility of an indirect "superexchange" mechanism involving one or more of the three types of Cu–Cu bridging linkages as the most probable alternative.

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(36) In this connection, however, it should be noted that aniline adducts of several copper(II) arylcarboxylates have been prepared and appear to have the dimeric copper(II) acetate structure with the aniline molecules occupying apical coordination sites.[11]

Of the three types of Cu–Cu bridge, two are monatomic oxygen bridges linking the apical coordination site of one copper atom with a basal site of an adjacent metal ion. Though recent work has clearly demonstrated that detectable copper–copper magnetic interactions can occur *via* this type of linkage, such interactions have invariably been substantially smaller than that observed in the present case.[37–40] Thus a recent tabulation of magnetic parameters for oxo-bridged dimers of this structure type[41] lists values of $2J$ ranging from -18 to $+40$ cm^{-1}. We thus consider it unlikely that the bridging oxygen atoms O(5) or O(7) could provide the major pathway for the observed magnetic coupling. In further support of this conclusion, we note the fact that the bridges formed by O(5) and O(7) are nonequivalent, with apical Cu–O distances of 2.318 (13) and 2.465 (14) Å, respectively. The conformity of the magnetic data to the dimer model would require that the two structurally different configurations be associated with interactions which are approximately equal, or which combine fortuitously to give the magnetic behavior of a dimer. Such an interpretation, though conceivable, is certainly unappealing. Finally, it should be noted that apical-to-basal Cu–O–Cu linkages, much like those observed in the present case, are found in anhydrous cupric propionate[35] and appear to have no significant influence on the magnetic properties of the anhydrous salt. That the observed pairwise interaction in the anhydrous cupric alkanoates occurs between the carboxylate-bridged copper atoms rather than between the oxo-bridged pairs is concluded from the very similar magnetic susceptibility behavior of the discrete dimer $[Cu(O_2CCH_3)_2\cdot H_2O]_2$ and the anhydrous salts.[5,42] We conclude that the magnetic susceptibility behavior of bis(propionato)-*p*-toluidinecopper(II) can best be accounted for by a pairwise interaction between Cu(1) and Cu(2) for which the principal pathway is an indirect one involving the triatomic carboxylate bridges. Again it must be emphasized that other coupling terms may well be present, but are likely to be much smaller than the principal mode of interaction.

Finally, it is important to note that copper(II) propionate·*p*-toluidine conforms to all of the criteria which have commonly been taken to infer for a cupric carboxylate adduct a structure of the dimeric copper(II) acetate hydrate type. These criteria include the $Cu(O_2CR)_2\cdot L$ stoichiometry, conformity of the temperature dependence of the magnetic susceptibility to eq 1, and the presence of an absorption band at *ca.* 3800 Å, both in the solid state and in solution. Clearly these criteria are insufficient in themselves to specify the dimeric copper(II) acetate structure and must be amended.

Acknowledgments. Support of this work by the National Science Foundation is gratefully acknowledged. We also thank Mr. Patrick Grant for his help with the neutron activation analysis.

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Synthesis and Structure of a Tetranuclear Zinc(II) Complex of *N*,*N*′-Dimethyl-*N*,*N*′-bis(β-mercaptoethyl)ethylenediamine

W. J. Hu, D. Barton, and S. J. Lippard*

Contribution from the Department of Chemistry, Columbia University,
New York, New York 10027.
Received May 30, 1972

Abstract: The preparation of a zinc derivative of the new ligand *N*,*N*′-dimethyl-*N*,*N*′-bis(β-mercaptoethyl)ethylenediamine is described. The molecular structure of a hydrate of the tetranuclear complex, $[Zn_2(C_8H_{18}N_2S_2)_2Cl_2]_2\cdot 2H_2O$, has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 11.874$ (3) Å, $b = 10.260$ (2) Å, $c = 14.260$ (3) Å, and $\beta = 113.92$ (1)°. The density of 1.782 g/cm^3 calculated on the basis of two formulas per unit cell is in agreement with the measured density 1.778 (3) g/cm^3. The structure was solved using 1156 independent, statistically significant reflections collected on a full-circle automated diffractometer. Refinement of all atoms including the water and methylene hydrogens led to a final value for the discrepancy index, R_1, of 0.054. The structure is a centrosymmetric array of four coplanar zinc atoms with four bridging mercaptide ligands. There are two types of zinc atoms, one with a strongly distorted tetrahedral N_2S_2 donor atom set, and the other with a regular tetrahedral Cl_2S_2 donor atom set. The lattice water is hydrogen bonded to chlorine atoms. The geometrical consequences of the sterically constraining ligand L are described.

In a study of the effect of steric strain on the electronic and redox properties of metal–sulfur complexes,[1] the ligand *N*,*N*′-dimethyl-*N*,*N*′-bis(β-mercaptoethyl)ethylenediamine (I) was designed.[2] The synthesis was achieved by mercaptoethylation of the parent diamine using ethylene monothiocarbonate.[3] In order to assess

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(2) Chemical control of this steric strain is synthetically possible by varying the number of methylene groups between the donor atoms in I.

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